(12) UK Patent Application (19) GB (11) 2 166 247 A

(43) Application published 30 Apr 1986

(21) Application No 8526063

(22) Date of filing 22 Oct 1985

(30) Priority data

(31) 8427004 (32) 25 Oct 1984 (33) GB

(51) INT CL[4]
G01N 27/12

(52) Domestic classification
G1N 19B2B 19B2Q 19B2X 19D11 19D12FO 19F1A 19F1B 24S
U1S 1482 1483 1484 1496 1497 1498 1499 1510 1511 G1N

(56) Documents cited
GB A 2149123
GB A 2149122
GB A 2149121
GB A 2149120
GB 1200439
EP A1 0022028

(58) Field of search
G1N
Selected US specifications from IPC sub-class G01N

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(54) Gas sensors

(57) A gas sensor suitable for use in gases and gaseous mixtures includes a gas sensitive material (1) which is capable of exhibiting a response in the form of an increase or a decrease in an electrical property of the material in the presence of a first gas and which is capable of exhibiting an opposite response in the presence of a second gas. A pair of electrodes (2), (3) may be provided in contact with the material (1) and the resistance, capacitance and or impedance of the material (1) measured. Various gas sensitive materials of various oxides are disclosed together with their response to various gases.

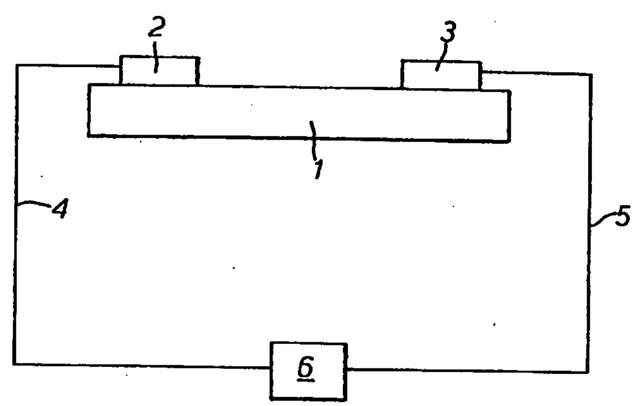

Fig.1.

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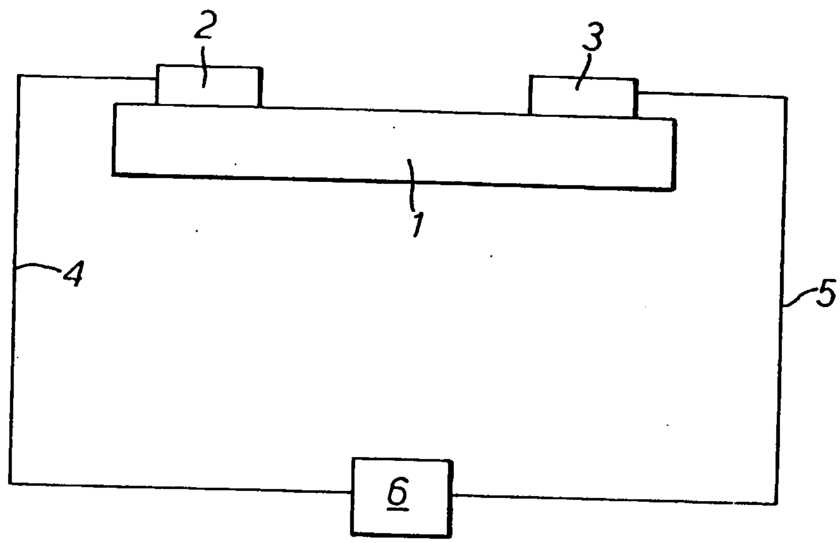

Fig.1.

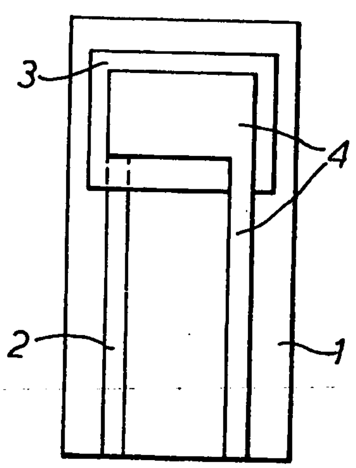

Fig.2.

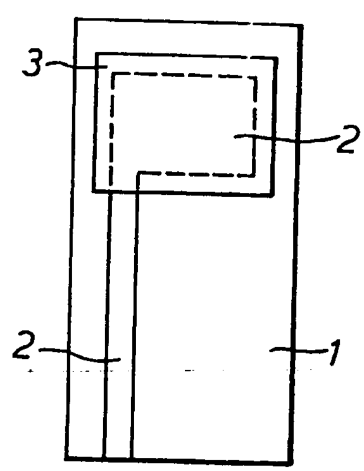

Fig.2a.

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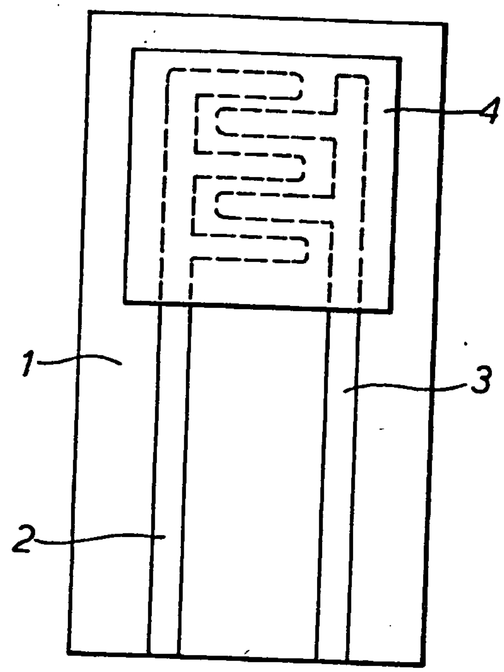

Fig.3.

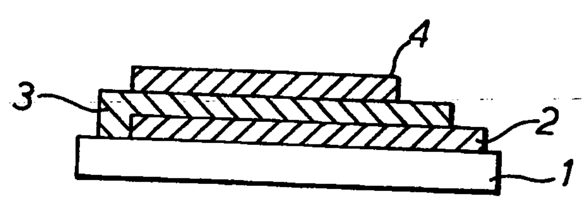

Fig.4.

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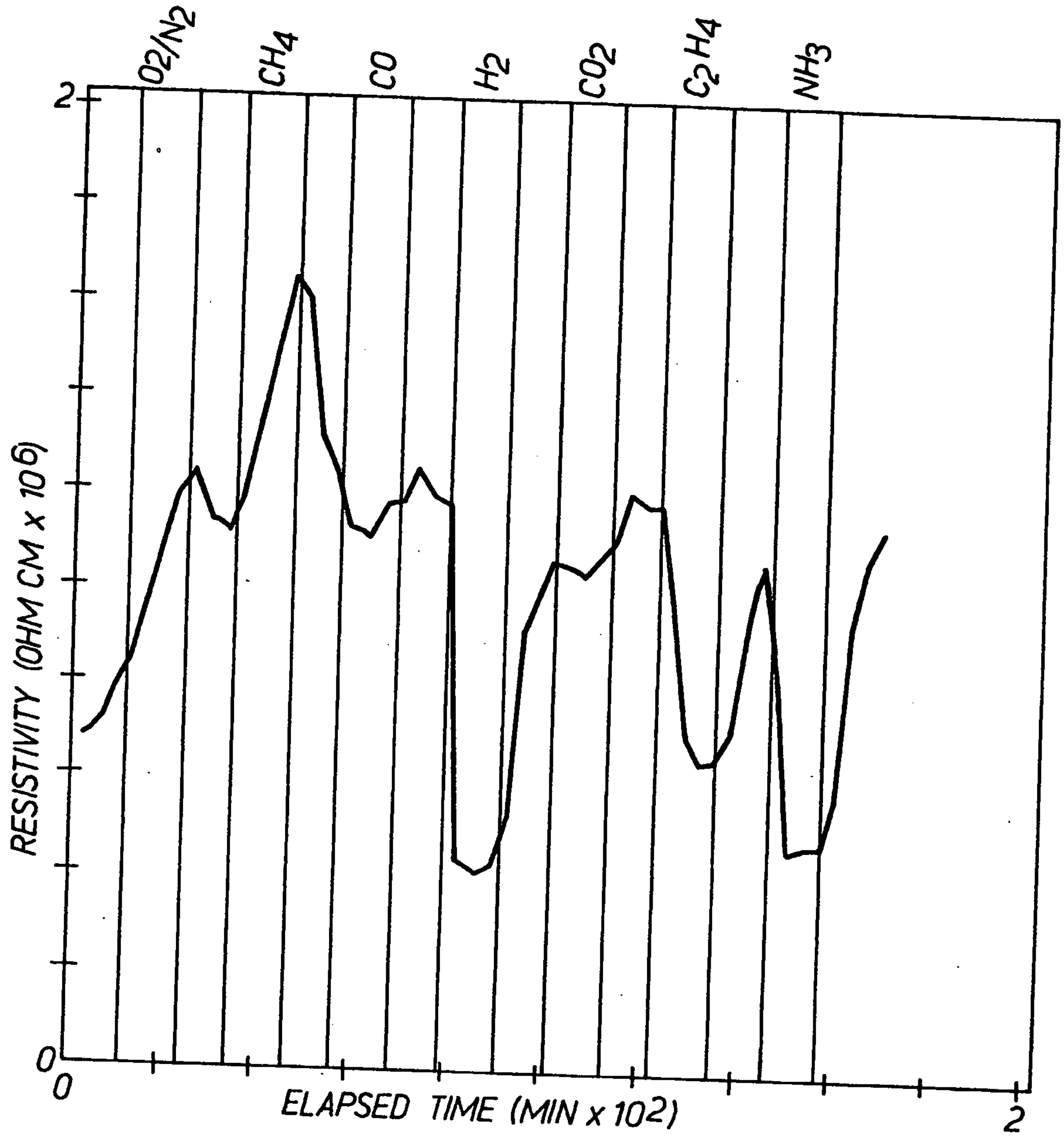

Fig.5.

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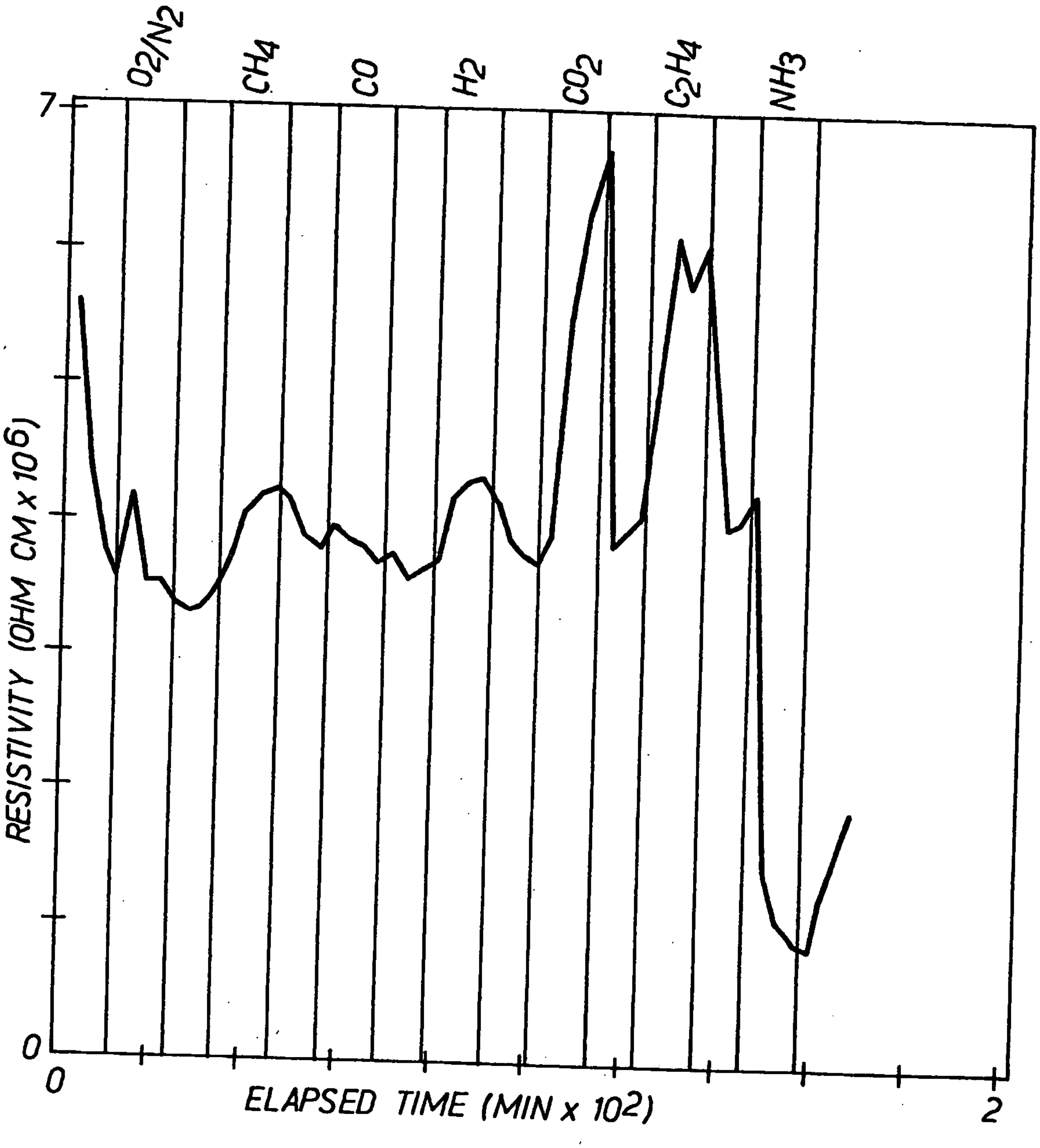

Fig. 6.

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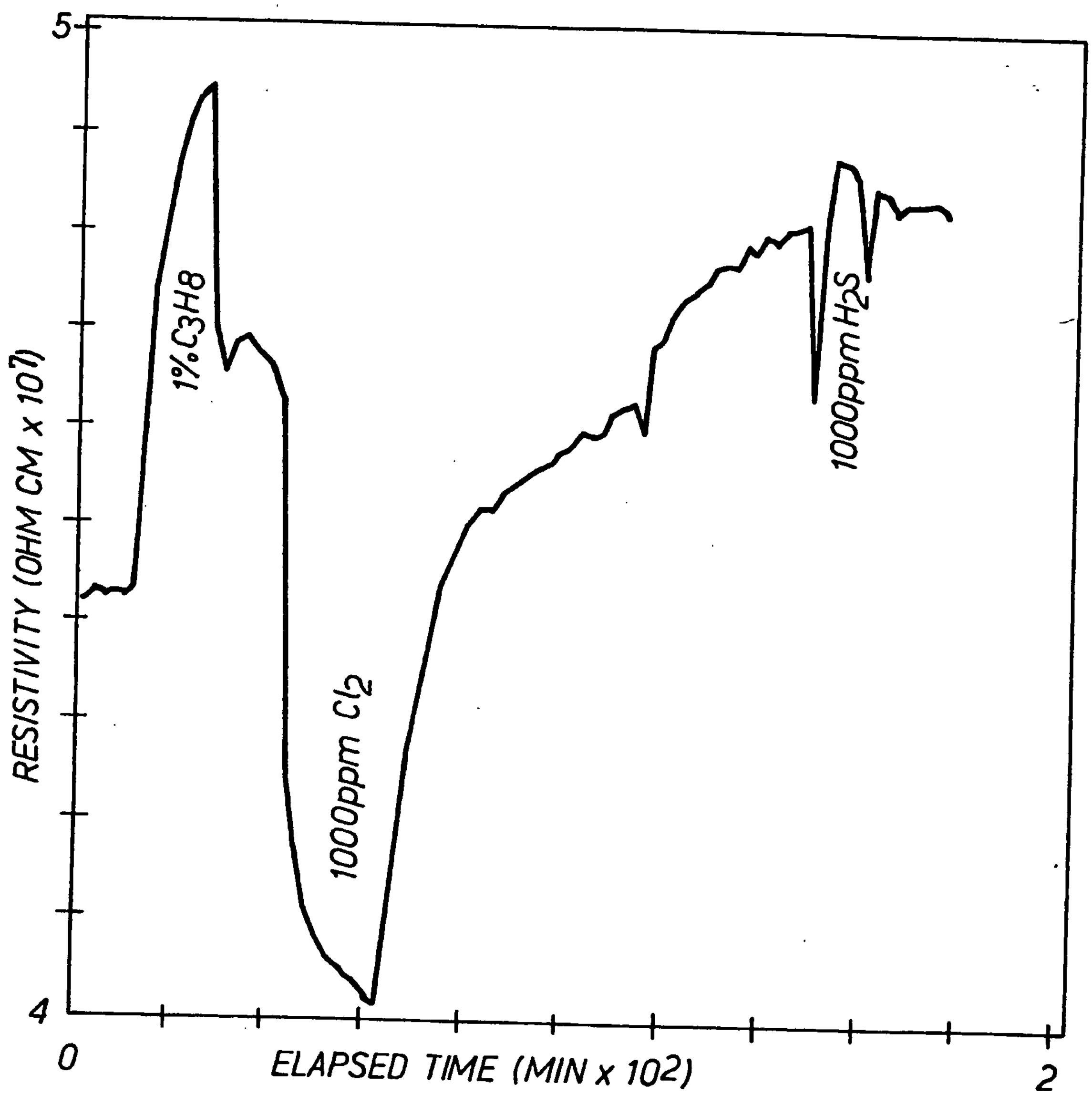

Fig.7.

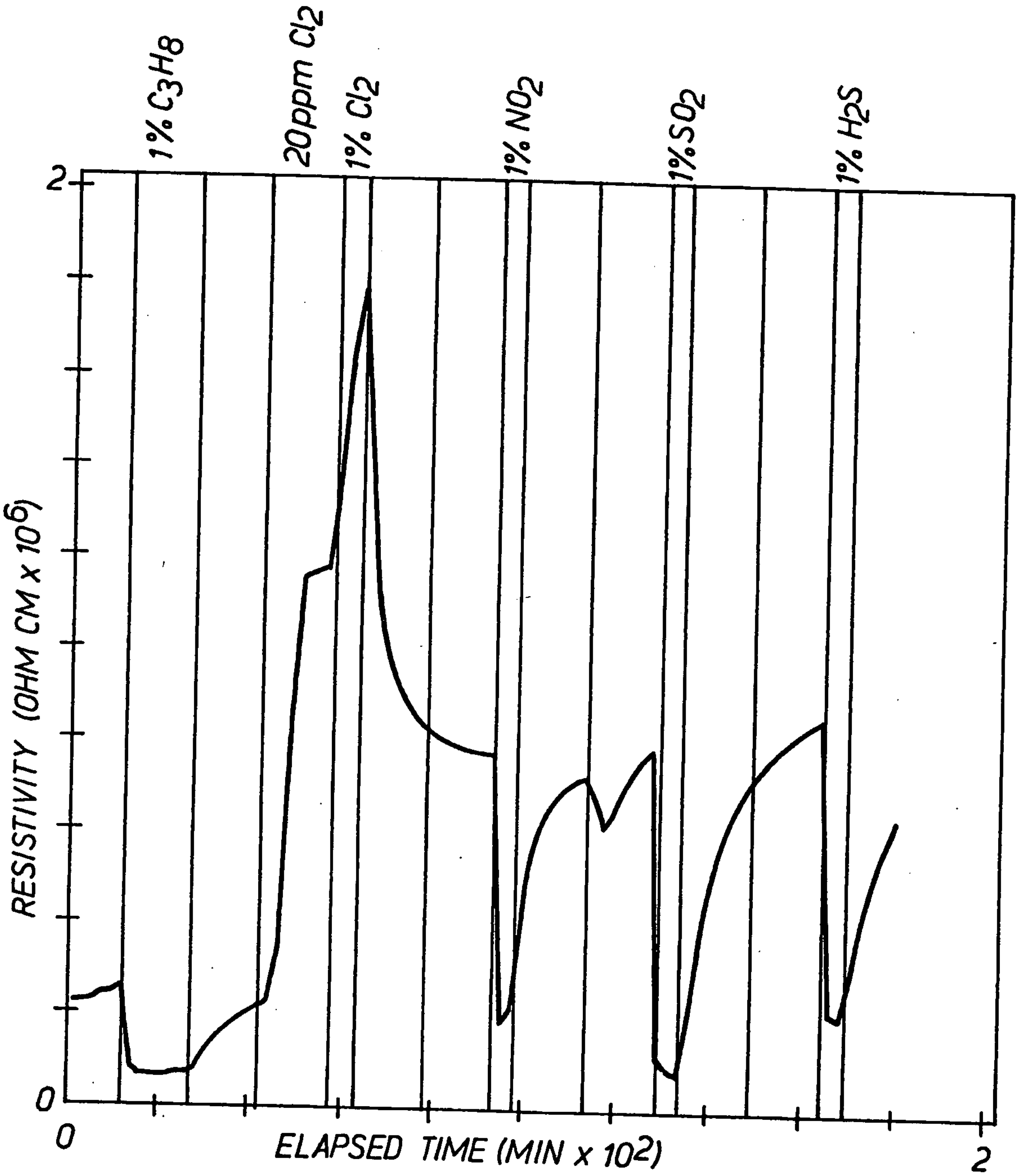
1% C_3H_8
20ppm Cl_2
1% Cl_2
1% NO_2
1% SO_2
1% H_2S
2
0
RESISTIVITY (OHM CM x 10^6)
0
ELAPSED TIME (MIN x 10^2)
2

Fig.8.

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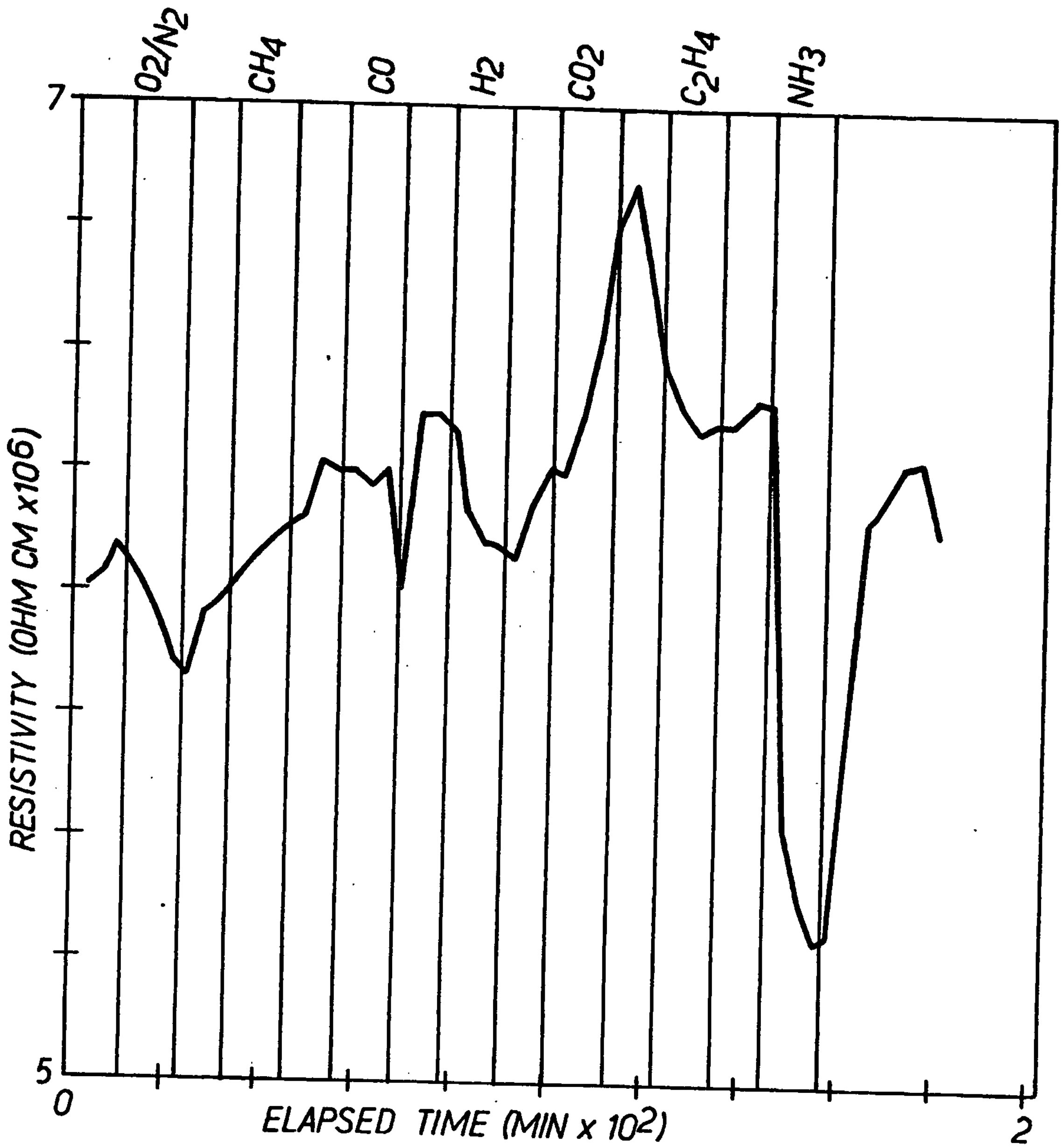

Fig.9.

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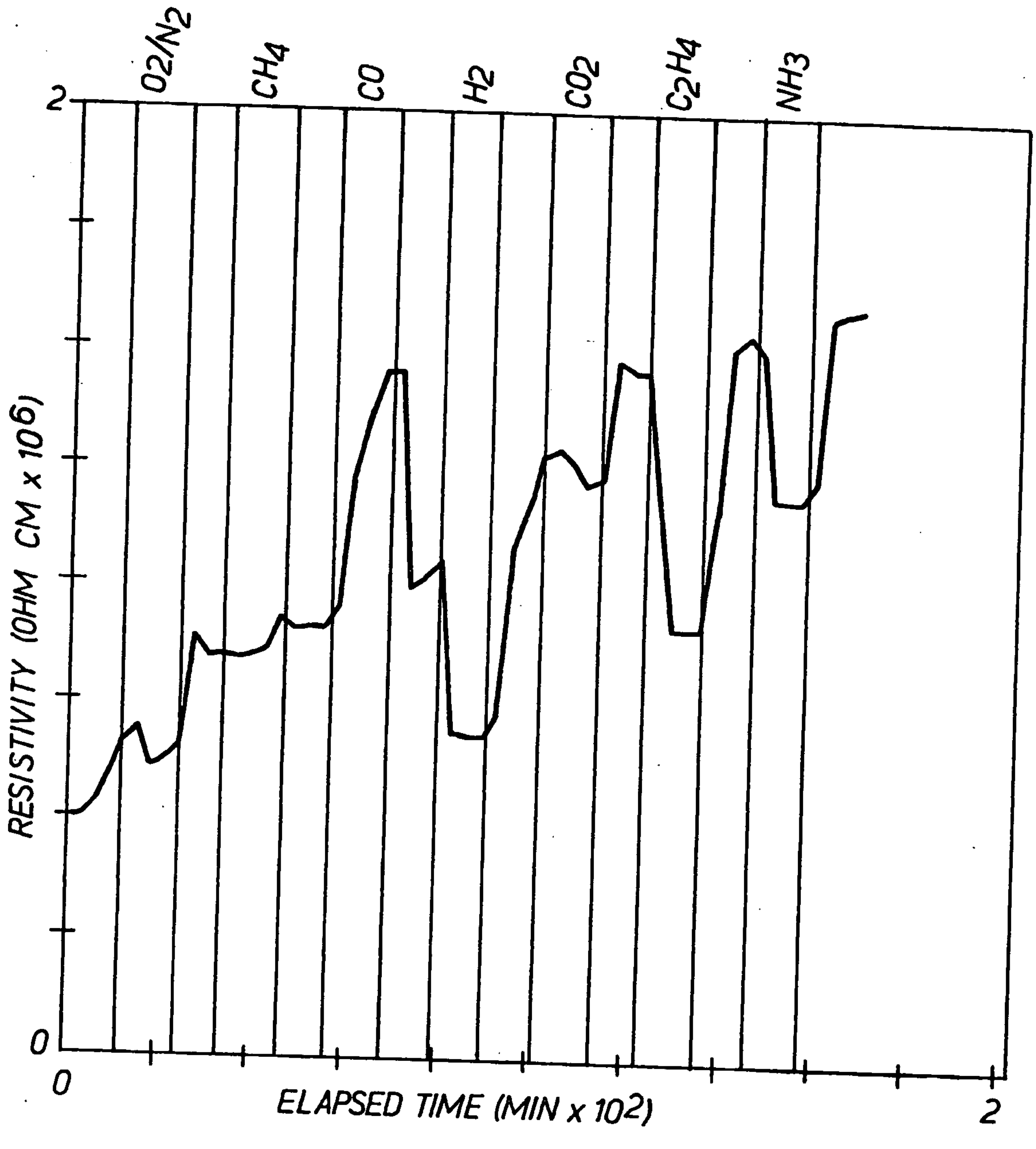

Fig. 10.

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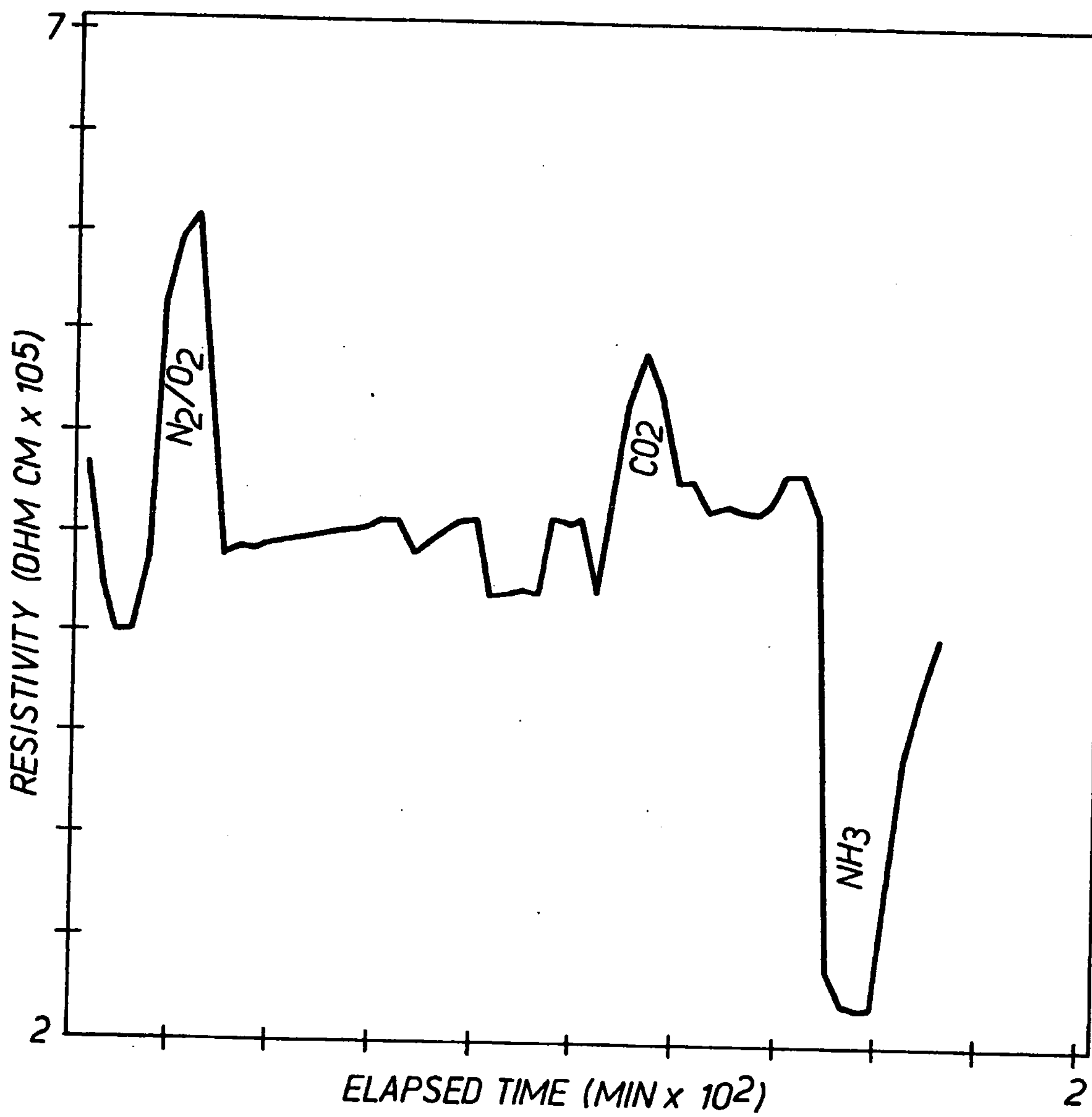

Fig.11.

SPECIFICATION

Improvements in or relating to sensors

The present invention relates to sensors and more particularly to sensors suitable for use in gases and gaseous mixtures.

According to one aspect of the present invention there is provided a sensor suitable for use in a gas or gaseous mixture which sensor includes a gas sensitive material (as hereinafter defined) which is capable of exhibiting a response in the form of an increase or a decrease in an electrical property of the material in the presence of a first gas and which is capable of exhibiting an opposite response in the presence of a second gas.

It will be appreciated that "opposite response" as used in this Specification means that the response of the material in the presence of the second gas is in the opposite sense to the response of the material in the presence of the first gas; thus, for example, if the material exhibits an increase in an electrical property in the presence of the first gas it will show a decrease in an electrical property in the presence of the second gas and vice versa.

In one embodiment of the present invention the gas sensitive material is provided with two or more electrodes in communication with the said gas sensitive material and said gas sensitive material is arranged so as to be capable of being contacted with a gas or gaseous mixture.

A sensor in accordance with the present invention may by used as a gas sensor in quantitative and/or qualitative determinations with gases and gaseous mixtures.

The gas sensitive material may be chosen, for example, so as to give a response in the presence of a chosen gas and an opposite response in all other gases likely to be encountered in a given situation.

The electrodes may be in direct communication with the gas sensitive material by being in contact therewith.

In this Specification the term "gas" embraces a gas as such and any material which may be present in a gaseous phase, one example of which is a vapour.

The gas sensitive material may be chosen for example so as to give a sensor suitable for discriminating between a pair of gases by being capable of exhibiting a response in one gas and an opposite response in the other.

Also, it will be appreciated that in this Specification the term "gas sensitive material" means a material which is gas (including vapour) sensitive in respect of an electrical property of the material.

It will be appreciated that the resistance and/or capacitance and/or impedance of the gas sensitive material depends upon the gas or gaseous mixture contacting the gas sensitive material. Thus, by measuring the resistance and/or capacitance and/or impedance of the gas sensitive material the composition of a gas or gaseous mixture can be sensed.

Since the resistance and/or capacitance and/or impedance of the gas sensitive material tends also to be temperature dependant, the sensor also preferably includes a temperature sensing means.

The sensor may also, optionally, include a heating means to enable operating temperature to be adjusted and/or contaminants to be burnt off if required.

It is to be understood that the sensitivity of a gas sensitive material may depend upon the composition of the gas sensitive material. Thus, by selection of the composition of the gas sensitive material its response to a particular gas or gases may be chosen.

Examples of gas sensitive materials which may be used to give a response in the presence of a first gas and an opposite response in the presence of a second gas are
WNb_2O_8, $BaTiO_3$, $LiFeSnO_4$, $KTaWO_6$,
$Ba_6Ti_2Nb_8$, $O_{30}Ba_6FeNb_9O_{30}$, $FeMoO_4$,
$BaSn_{2.8}Cr_{1.2}O_8$, $TiNb_2O_7$,
$CuNb_2O_6$,$BaSn_{2.8}Al_{1.2}O_8$,
ZrO_2(3 mole % Y_2O_3),
$Ca_{0.1}La_{0.9}FeO_3$, $BaTi_{0.95}Sn_{0.05}O_3$,
$BaSn_{0.72}Ce_{0.3}O_3$.

The resistance and/or conductance and/or impedance may be measured directly. Alternatively, the measurement may be carried out indirectly by incorporating the sensor in a feedback circuit of an oscillator such that the oscillator frequently varies with composition of the gas or gaseous mixture. Gas composition may then be determined using an electronic counter. The signal thus produced may be used to modulate a radio signal and thereby be transmitted over a distance (e.g. by telemetry or as a pulse train along an optical fibre).

Examples of gases which have shown responses using a sensor in accordance with the present invention are H_2, C_2H_4, NH_3, CO_2, O_2, C_3H_8, CH_4, CO, Cl_2, NO_2, SO_2 and H_2S.

According to another aspect of the present invention there is provided a method for effecting determinations in a gas or gaseous mixture which comprises contacting a sensor with the gas or gaseous mixture and measuring the electrical response of the sensor, said sensor including a gas sensitive material which is capable of exhibiting a response in the form of an increase or a decrease in an electrical property of the material in the presence of a first gas and which is capable of exhibiting an opposite response

in the presence of a second gas.

In one embodiment of the immediately preceding aspect of the present invention the gas sensitive material (as hereinbefore defined), has two or more electrodes in communication with the said gas sensitive material, and the gas sensitive material and the electrodes are in contact with the same gas or gaseous mixture.

It is preferred that the gas sensitive material has porosity to give a satisfactory surface area for contact with a gas or gaseous mixture when in use.

The gas sensitive material may, for example, be prepared from a mixture of powders of appropriate starting materials.

It will be understood that "appropriate starting materials" in this Specification means materials which can be processed to give the required gas sensitive material (e.g. where the gas sensitive material is to contain certain elements such as Ba, Sn and Nb appropriate starting materials may be powdered compounds of Ba, Sn and Nb. Oxides and oxide precursors are examples of materials from which the gas sensitive material may be prepared. The oxides or oxide precursors may be, for example, of laboratory reagent grade. Examples of oxide precursors are carbonates, nitrates, oxalates and acetates that may be converted to the corresponding oxide.

Oxides and oxide precursors may optionally be prepared by a gel process such as a sol-gel process or a gel precipitation process.

In preparing the gas sensitive material, by way of example, finely ground powders of the appropriate starting materials in appropriate proportions (i.e. in proportions appropriate to the desired composition of the desired gas sensitive material) may be thoroughly mixed in suspension (e.g. in acetone) by using a mill apparatus in which materials are ground, mixed and dispensed (e.g. by use of small alumina ceramic balls agitated in a steel pot by a steel blade).

Mixing time and speed may be minimised to avoid unnecessary contamination of the starting materials.

After mixing the resulting powder mixture may be dried and calcined (e.g. for ~ 16 hours) at a temperature in the range 700 - 1300° (conveniently ~ 800°C or ~ 1200°C) depending upon the melting temperature of the starting materials or the particular composition of gas sensitive material being prepared.

The product resulting from calcination, which may be in the form of a cake, may be ground as required to give a fine powder. (If required, grinding and calcination may be repeated several times in order to obtain a more fully reacted product powder).

Subsequently the fine powder may be pressed (e.g. with the optional addition of a binder, such as a solution of starch or PVA) into any suitable shape (e.g. a pellet).

The pressing may be followed by firing (e.g. at the same temperature as the calcination step(s) described above, or at a somewhat higher temperature, for ~ 16 hours).

In addition to assisting binding the powder into the desired shape the binder also burns out during the firing stage and may give rise to porosity.

As an alternative to mixing powders in suspension a powder mixture for subsequent calcination may be prepared, for example, by spray drying a solution (e.g. an aqueous solution) of appropriate starting materials (e.g. metal oxalates, metal acetates or metal nitrates) in appropriate proportions.

Electrodes may be applied to the gas sensitive material once prepared in any suitable manner. For example, electrodes (e.g. gold electrodes) may be applied by means of screen printing or sputtering.

Alternatively to preparing a sensor by forming a pellet and applying electrodes as disclosed above, a sensor in accordance with the present invention may be formed in any suitable manner. Thus, for example, a parallel plate configuration may be fabricated by applying a first electrode (e.g. of gold) to an insulating substrate (e.g. by screen printing or sputtering), forming a gas sensitive material layer covering at least a portion of the first electrode (e.g. by deposition, for example by screen printing or doctor-blading, from a suspension or a colloidal dispersion and firing at a temperature in the range 450 - 950°C to promote adhesion and mechanical integrity) and forming a second electrode (e.g. of gold) on the gas sensitive material layer (e.g. by screen printing or sputtering).

The second electrode is preferably permeable to facilitate access of gas or gaseous mixture in which the sensor is to be used to the gas sensitive material layer.

By way of further example, a coplanar configuration can be used in the preparation of a sensor in accordance with the present invention.

In such a coplanar configuration interdigitated electrodes (e.g. of gold) may be formed on an insulating substrate (e.g. by screen printing, or by sputtering, or by photolithography and etching). The interdigitated electrodes are subsequently covered with a gas sensitive material layer (e.g. by means of deposition, for example by screen printing or doctor-blading, from a suspension or a colloidal dispersion) and firing at a temperature in the range of 450 - 950°C to promote adhesion and mechanical integrity.

Sensors in accordance with the present invention fabricated in a coplanar configuration may include another layer or layers interposed between the gas sensitive material layer and the electrodes. By way of example, an interposed layer may be a layer of a dielectric material, or a layer for promoting adhesion of the gas sensitive material (e.g. a layer of glass material or a layer fabricated from a powder prepared from a gel). By way of further example, a layer for promoting adhesion may be interposed between a dielectric layer and the gas sensitive material layer.

By way of further example, sensors in accordance with the present invention may be fabricated by depositing a gas sensitive material layer on electrodes of any suitable configuration for example those fabricated in the form of "wander tracks". By way of yet further example, a gas sensitive material layer may be deposited onto a semi-conductor device such as a field effect transistor, MOS capacitor or gate-controlled diode.

The present invention will now be further described with reference to Table I which gives Examples of gas sensitive materials in accordance with the present invention together with resistance results obtained when contacted with certain gases in air.

In the case of the Examples listed in Table I the gas sensitive material in each case comprised a pellet (~ 2mm thich and 1cm in diameter); sputtered gold electrodes were used on opposing faces of the pellet and the sensor constituted thereby was mounted between gold foils in a furnace tube in a flowing gas stream (of chosen composition) while electrical measurements were made.

Also in the case of the Examples listed in Table I in each case the gas sensitive material was prepared by mixing appropriate finely ground starting materials in suspension in acetone in a mill, drying, calining (at a temperature in the range 700 - 1300°C for ~ 16 hours, grinding to a fine powder and pressing and firing for ~ 16 hours (at a preferred temperature in the range 800°C to 1000°C) to give pellets.

TABLE 1:

Gas Sensitive Material	*Gases in which resistance decreases*	*Gases in which resistance increases*	*Sensor Operating Temp (°C)*
WNb_2O_8	H_2,C_2H_4,NH_3	CH_4	500
$BaTiO_3$	NH_3	CH_4,H_2,CO_2, C_2H_4	500
$LiFeSnO_4$	CO_2	red O_2,CO	500
$KTaWO_6$	red O_2,CH_4,CO, H_2,CO_2,C_2H_4	NH_3	200
$Ba_6Ti_2NbO_{30}$	Cl_2,H_2,C_2H_4, NH_3	C_3H_8	500
$Ba_6FeNb_9O_{30}$	C_3H_8,NO_2,SO_2, H_2S	Cl_2	500
$FeMoO_4$	H_2,NH_3	CO_2	200
$BaSn_{2.8}Cr_{1.2}O_8(SnO_2)$	red O_2,H_2,CO_2, C_2H_4, NH_3	CO	500
$BaSn_{2.8}Al_{1.2}O_8(SnO_2)$	red O_2,CH_4,H_2, CO_2,C_2H_4,NH_3	CO	500
ZrO_2(^{3m}/o Y_2O_3)	H_2	red O_2,CH_4, CO, CO_2	500
$Ca_{0.1}La_{0.9}FeO_3$	NH_3	red O_2,CO_2	500
$TiNb_2O_7$	CO,H_2,C_2H_4,NH_3, Cl_2	C_3H_8	500

TABLE 1 (continued)

Gas Sensitive Material	*Gases in which resistance decreases*	*Gases in which resistance increases*	*Sensor Operating Temp (°C)*
$CuNb_2O_6$	H_2,C_2H_4,NH_3, C_3H_8,SO_2,H_2S	Cl_2	500
$BaTi_{0.95}Sn_{0.05}O_3$	NH_3	CH_4, H_2, C_2H_4	500
$BaSn_{0.7}Ce_{0.3}O_3$	NH_3	CH_4, CO, C_2H_4, red O_2	500

The present invention will now be further described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a diagrammatic representation of one form of sensor in accordance with the present invention;

Figure 2 and *Figure 2a* represent diagrammatically a parallel plate sensor in accordance with the present invention and a partially completed parallel plate sensor respectively;

Figure 3 is a diagrammatic representation of a coplanar sensor in accordance with the present invention;

Figure 4 is a diagrammatic representation of a further form of sensor in accordance with the present invention;

Figure 5 is the response, in terms of resistance at IKHz and time, of a sensor of the form used in the Examples given in Table I at approximately 500°C with the gases and gaseous mixtures indicated using WNb_2O_8 as the gas sensitive material;

Figure 6 is the response, in terms of resistance at IKHz and time, of a sensor of the form used in the Examples given in Table I at ~ 500°C with the gases and gaseous mixtures indicated using $BaTiO_3$ as the gas sensitive material;

Figure 7 is the response, in terms of resistance at 10 KHz and time, of a sensor of the form used in the Examples given in Table I at approximately 500°C with the gases indicated (in air) using $Ba_6Ti_2Nb_8O_{30}$ as the gas sensitive material.

Figure 8 is the response, in terms of resistance at 10 KHz and time, of a sensor of the form used in the Examples given in Table I at approximately 500°C with the gas indicated (in air) using $Ba_6FeNb_9O_{30}$ as the gas sensitive material;

Figure 9 is the response, in terms of resistance at 1KHz and time, of a sensor of the form used in the Examples given in Table I at approximately 200°C with the gas indicated (in air) using $FeMoO_4$ as the gas sensitive material;

Figure 10 is the response, in terms of resistance at 1KHz and time, of a sensor of the form used in the Examples given in Table I at approximately 500°C with the gas indicated (in air) using $BaSn_{2.8}Cr_{1.2}O_8$ (x-ray) main phase SnO_2) and

Figure 11 is the response, in terms of resistance used in the Examples given in Table I at approximately 500°C with the gas indicated using $Ca_{0.1}La_{0.9}FeO_3$.

Referring now to Figure 1 of the drawings there is shown a sensor comprising a gas sensitive material 1 and, in contact with the gas sensitive material 1 gold electrodes 2 and 3. (The gas sensitive material may be carried by a substrate (e.g. of alumina) (not shown)).

Conductors 4 and 5 are provided to connect the electrodes 2 and 3 respectively to electrical measuring means 6 for measuring the resistance and/or capacitance and/or impedance of the gas sensitive material 1.

In operation a gas or gaseous mixture is contacted with the gas sensitive material 1.

The resistance and/or capacitance and or impedance is measured by the electrical measuring means 6. Changes in the composition of the gas or gaseous mixture which result in a change of resistance and/or capacitance and/or impedance are observed as changes in the resistance and/or capacitance and/or impedance recorded by the measuring means 6.

Referring now to Figure 2 of the drawings there is shown (in plan view) an insulating substrate 1 (e.g. an alumina ceramic tile) upon which is formed a first electrode 2 (e.g. of gold), a gas sensitive material layer 3 comprising a gas sensitive material in accordance with the present invention and a second electrode 4 (e.g. of gold).

A parallel plate sensor as shown in Figure 2 may be fabricated by applying the first electrode 2 (e.g. of

gold) to the insulating substrate 1 (e.g. by screen printing or sputtering), forming a gas sensitive material layer 3 by deposition, for example by screen printing or doctor-blading, from a suspension or a colloidal dispersion and firing at a temperature in the range 450 - 950°C to promote adhesion and mechanical integrity) and forming a second electrode 4 (e.g. of gold) on the gas sensitive material layer 3, (e.g. by screen printing or sputtering).

To facilitate understanding of the construction of the sensor of Figure 2 reference may be made to Figure 2a which shows a parallel plate sensor of the type shown in the Figure 2 partially completed inasmuch as the second electrode 4 has not been formed. Figure 2a thus shows the insulating substrate 1, the first electrode 2 and the gas sensitive material layer 3 and it can be seen that the portion of the first electrode 2 covered by the gas sensitive material layer 3 may extend in area to substantially the same extent as the second electrode 4.

In operation the first electrode 2 and second electrode 4 are connected to an electrical measuring means (not shown) for measuring the resistance and/or capacitance and/or impedance of the gas sensitive material layer 3 and the sensor is contacted with a gas or gaseous mixture. The resistance and/or capacitance and/or impedance is measured by the electrical measuring means and changes in the composition of the gas or gaseous mixture which result in a change of resistance and/or capacitance and/or impedance are observed as changes in the resistance and/or capacitance and/or impedance recorded by the measuring means.

Referring now to Figure 3 there is shown (plan view) an insulating substrate 1 (e.g. an alumina ceramic tile) upon which are formed electrodes 2 and 3 (e.g. both of gold), and a gas sensitive material layer 4 (comprising a gas sensitive material in accordance with the present and 3. It will be seen from the lines shown in dotted form in Figure 3 the portions of the first electrode 2 and second electrode 3 covered by the gas sensitive material layer 4 are interdigitated.

The first electrode 2 and the second electrode 3 may be provided on the insulating substrate 1 by any suitable method. For example the methods disclosed for providing electrodes 2 and 4 in the parallel plate sensor described hereinbefore with reference to Figure 2 and Figure 2a may be used.

The gas sensitive material layer 4 shown in Figure 3 may be prepared by any suitable method. For example the methods disclosed for preparing gas sensitive material layer 2 in Figure 2 and Figure 2a may be used.

Referring now to Figure 4 of the drawings there is shown a diagrammatic representation in cross-section of a gas sensor having an insulating substrate 1, electrodes represented as 2, a dielectric layer 3 and a gas sensitive material layer 4.

The electrodes 2 and the layers 3 and 4 may be prepared by any suitable method. Thus, for example, screen printing or sputtering or photolithography and etching may be used as is appropriate.

Referring now to Figures 5 to 11 of the drawings there are shown respectively the response (as change of resistance) of WNb_2O_8, $BaTiO_3$, $Ba_6Ti_2Nb_8O_{30}$, Ba_6FeNbO_{30}, $FeMoO_4$, $Ba_6Sn_{2.8}Cr_{1.2}O_8$ and $Ca_{0.1}La_{0.9}FeO_3$ gas sensitive materials in the presence of the gases and gaseous mixtures indicated.

CLAIMS

1. A sensor suitable for use in a gas or gaseous mixture which sensor includes a gas sensitive material (as hereinbefore defined) which is capable of exhibiting a response in the form of an increase or a decrease in an electrical property of the material in the presence of a first gas and which is capable of exhibiting an opposite response in the presence of a second gas.

2. A sensor as claimed in Claim 1 wherein the gas sensitive material is provided with two or more electrodes in communication with the said gas sensitive material and said gas sensitive material is arranged so as to be capable of being contacted with a gas or gaseous mixture.

3. A sensor as claimed in Claim 1 or Claim 2 wherein the gas sensitive material is such as to give a response in the presence of a chosen gas and an opposite response in all other gases likely to be encountered in a given situation.

4. A sensor as claimed in any one of the preceding claims wherein the electrodes are in direct communication with the gas sensitive material be being in contact therewith.

5. A sensor as claimed in any one of the preceding claims wherein the sensor indicates a temperature sensing means.

6. A sensor as claimed in any one of the preceding claims wherein the sensor includes a heating means.

7. A sensor as claimed in any one of the preceding claims wherein the gas sensitive material comprises

WNb_2O_8, $BaTiO_3$, $LiFeSnO_4$, $KTaWO_6$,
$Ba_6Ti_2Nb_8$, O_{30}, $Ba_6FeNb_9O_{30}$, $FeMoO_4$,
$BaSn_{2.8}Cr_{1.2}O_8$, $TiNb_2O_7$,
$CuNb_2O_6$,$BaSn_{2.8}Al_{1.2}O_8$,
ZrO_2(3 mole % Y_2O_3),
$Ca_{0.1}La_{0.9}FeO_3$, $BaTi_{0.95}Sn_{0.05}O_3$,
$BaSn_{0.72}Ce_{0.3}O_3$.

8. A method for effecting determination in a gas or gaseous mixture which comprises contacting a sensor with the gas or gaseous mixture and measuring the electrical response of the sensor, said sensor including a gas sensitive material which is capable of exhibiting a response in the form of an increase or a decrease in an electrical property of the material in the presence of a first gas and which is capable of exhibiting an opposite response in the presence of a second gas.

9. A method as claimed in Claim 8 wherein two or more electrodes are provided in communication with the said gas sensitive material, and the gas sensitive material and the electrodes are in contact with the same gas or gaseous mixture.

10. A method as claimed in Claim 8 or 9 wherein the gas sensitive material has porosity to give surface area for contact with a gas or gaseous mixture when in use.

11. A method as claimed in any one of Claims 8, 9 or 10 wherein the resistance of the sensor is measured.

12. A method as claimed in any one of Claims 8, 9 or 10 wherein the capacitance of the sensor is measured.

13. A method as claimed in any one of Claims 8, 9 or 10 wherein the impedance of the sensor is measured.

14. A method as claimed in any one of Claims 8, 9, 10, 11, 12 or 13 wherein the sensor detects H_2, C_2H_4, NH_3, CO_2, O_2, C_3H_8, CH_4, CO, Cl_2, NO_2, SO_2, or H_2S.

15. A sensor substantially as hereinbefore described with reference to any one of the Figures 1, 2, 2a, 3 or 4 of the accompanying drawings.

16. A method for preparing a sensor substantially as hereinbefore described with reference to any one of the Figures 2, 2a, 3 or 4 of the accompanying drawings.

17. A method for effecting determination in a gas or gaseous mixture substantially as hereinbefore described with reference to any one of the Figures 1, 2, 2a, 3 or 4 of the accompanying drawings.

Printed in the UK for HMSO, D8818935, 3/86, 7102.
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